Density, Speed of Sound, and Viscosity of Binary Mixtures of Poly(propylene glycol) 400 + Ethanol and + 2-Propanol at Different Temperatures

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The density and speed of sound of the solutions of poly(propylene glycol) 400, in ethanol and 2-propanol at T = (288.15 to 328.15) K, and dynamic viscosity of these solutions at T = (298.15 to 328.15) K have been measured experimentally over the entire range of compositions and atmospheric pressure. From these experimental data, the excess molar volume, V_{m}^{E} , excess molar isentropic compression, $\kappa_{\text{s,m}}^{\text{E}}$, and deviation of logarithm of viscosity, $\Delta \ln \eta$, have been determined for each composition. V_{m}^{E} , $\kappa_{\text{s,m}}^{\text{E}}$, and viscosity data have been adequately fitted to the Redlich–Kister and NRTL models.

Introduction

Knowledge of volumetric and acoustical properties of polymer solutions has been proven to be a very useful tool in evaluating the structural interactions occurring in these solutions. In this respect, the isentropic compressibility and excess molar volume evaluated from sound velocity and density measurements have been used to determine the structure and the nature of molecular interactions in aqueous and nonaqueous solutions of polymers. Knowledge of the viscosity of polymer solutions is important for practical and theoretical purposes. Viscosity of polymer solutions provides an invaluable type of data in polymer research, development, and engineering. Furthermore, the simultaneous investigation of viscosity and volume effects on mixing can be a powerful tool for the characterization of intermolecular interactions present in these mixtures.

In recent years, numerous studies have been carried out on mixtures containing poly(propylene glycols), PPGs. PPG is used in many formulations for polyurethanes. It is used as a rheology modifier,¹ in solid tires, in automobile seats,² in foams,³ and in membranes.⁴

This work is a continuation of our studies on the determination of the density, speed of sound, and dynamic viscosity of the polymer + alcohol systems.^{5–7}

Experimental Section

PPG400 was obtained from Fluka. The number average molar mass M_n of this polymer was determined by a cryoscopic osmometer (Osmomat model 030). For this purpose, freezing point depression measurements on PPG400 + H₂O were carried out in different concentrations, and a $\Delta T/K_sC$ vs C curve was plotted (ΔT , C, and K_s are the freezing point depression, concentration of samples, and cryoscopic constant, respectively). The intercept of this curve is $1/M_n$, from which M_n for this polymer was found to be 401 g·mol⁻¹. Ethanol (minimum mass fraction purity 0.998) and 2-propanol (minimum mass fraction purity 0.995) were obtained from Merck and used without further purification. Double distilled, deionized water was used. The solutions were prepared by mass using an analytical balance

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Figure 1. Experimental and calculated excess molar volume, $V_{\rm m}^{\rm E}$, plotted against mole fraction of PPG, x_2 , at 298.15 K: \diamond , ethanol + PPG400 system; *, 2-propanol + PPG400 system; -, Redlich-Kister polynomial; - -, NRTL model.

(Shimatzu, 321-34553, Shimatzu Co., Japan) with an uncertainty of $\pm 1 \cdot 10^{-7}$ kg.

Density and speed of sound data were continuously measured using a commercial density and speed of sound measurement apparatus (Anton Paar DSA 5000 densimeter and speed of sound analyzer). Details of the experimental setup and measuring procedure have been given elsewhere.⁸ In each measurement, the uncertainty of density and speed of sound were $\pm 3.0 \cdot 10^{-6}$ g·cm⁻³ and ± 0.5 m·s⁻¹, respectively.

The viscosity was determined by a Setavis Kinematic Viscometer-83541-3, England, as described previously.⁹ The uncertainty for the dynamic viscosity determination was estimated to be $\pm 0.5 \%$.

Density, speed of sound, and viscosity values of the pure components are given in Table 1 at different temperatures and compared with the literature values.



Figure 2. Experimental and calculated excess molar isentropic compression, $\kappa_{s,m}^{E}$, plotted against mole fraction of PPG, x_2 , at 298.15 K: \diamond , ethanol + PPG400 system; *, 2-propanol + PPG400 system; -, Redlich-Kister polynomial; - -, NRTL model.



Figure 3. Experimental and calculated viscosity, η , plotted against mole fraction of PPG, x_2 , for the ethanol + PPG400 system (a) and the 2-propanol + PPG400 system (b) at different temperatures: \blacktriangle , 298.15 K; \bigstar , 308.15 K; \ast , 318.15 K; \triangle , 328.15 K; \neg , Redlich-Kister equation; - -, NRTL model.

Table 1. Density, *d*, Speed of Sound, *u*, and Dynamic Viscosity, η , for Pure Components at T = (288.15 to 328.15) K

	Т	d	и	η
component	K	g•cm ⁻³	$m \cdot s^{-1}$	mPa•s
ethanol	288.15	0.79364	1177.47	
	298.15	0.78510	1143.49	1.0930
		0.78522^{13}	1143.10^{6}	1.077^{13}
		0.785085^{6}		1.084^{14}
	308.15	0.77643	1109.69	0.902
		0.77551^{14}	1111^{14}	0.903^{14}
		0.77726^{15}		
	318.15	0.76762	1076.32	0.759
	328.15	0.75860	1043.07	0.644
2-propanol	288.15	0.78912	1173.73	
		0.7891^{16}		
	298.15	0.78088	1138.94	2.089
		0.780824^{6}	1138.87^{6}	2.036^{17}
		0.7809^{16}	1141^{15}	2.045^{18}
	308.15	0.77227	1104.04	1.564
		0.77275^{15}		1.521^{15}
	318.15	0.76330	1068.72	1.192
		0.7635^{16}		1.191^{16}
	328.15	0.75392	1032.81	0.942
poly(propylene glycol) (PPG400)	288.15	1.01115	1399.74	
gijeei) (11 0 100)		1.011860^{5}	1400.58^{5}	
	298.15	1.00352	1365.85	70.435
		1.003929^{5}	1366.70^{5}	
	308.15	0.99554	1332.91	38.266
		0.995937 ⁵	1333.64 ⁵	
	318.15	0.98751	1300.72	24.700
	328.15	0.97950	1269.25	16.342

Results and Discussion

The experimental density, *d*, and speed of sound, *u*, data for ethanol + PPG and 2-propanol + PPG systems, as a function of PPG mole fraction, x_2 , at T = (288.15 to 328.15) K are collected in Table 2.

Values of the excess molar volume, $V_{\rm m}^{\rm E}$, and excess molar isentropic compression, $\kappa_{\rm s,m}^{\rm E}$, were calculated by the following equations

$$V_{\rm m}^{\rm E} = \sum_{i=1}^{2} x_i M_i \left[\frac{1}{d} - \frac{1}{d_i} \right] \tag{1}$$

$$\kappa_{\rm s,m}^{\rm E} = \sum_{i=1}^{2} x_i M_i \left[\frac{1}{(du)^2} - \frac{1}{(d_i u_i)^2} \right]$$
(2)

where *x* is the mole fraction; *M* is the molar mass; and subscripts 1 and 2 stand for solvent and polymer, respectively. The calculated $V_{\rm m}^{\rm E}$ and $\kappa_{\rm s,m}^{\rm E}$ values for ethanol + PPG and 2-propanol + PPG systems have been plotted versus the mole fraction of polymer, x_2 , in Figures 1 and 2 at 298.15 K as examples, respectively. Figures 1 and 2 show that both the $V_{\rm m}^{\rm E}$ and $\kappa_{\rm s,m}^{\rm E}$ are negative and become more negative when temperature increases. The negative values of $V_{\rm m}^{\rm E}$ and $\kappa_{\rm s,m}^{\rm E}$ for studied mixtures can be explained as a cumulative manifestation of the various types of intermolecular interactions between the components.

The deviation of logarithm of viscosity can be calculated as

$$\Delta \ln \eta = \ln \eta - \sum_{i=1}^{2} x_i \ln(\eta_i)$$
(3)

where η_i is the dynamic viscosity of the pure component *i*. The experimental dynamic viscosity, η , data for ethanol + PPG and 2-propanol + PPG systems, as a function of PPG mole fraction,

Table 2. Density and Speed of Sound of Binary Mixtures Containing Ethanol + PPG400 and 2-Propanol + PPG400 at Different Temperatures

<i>x</i> ₂	$d (g \cdot cm^{-3})$	$(\mathbf{m} \cdot \mathbf{s}^{-1})$	<i>x</i> ₂	d (g·cm ⁻³)	$(\mathbf{m} \cdot \mathbf{s}^{-1})$	<i>x</i> ₂	d (g·cm ⁻³)	$(\mathbf{m} \cdot \mathbf{s}^{-1})$	<i>x</i> ₂	$d (g \cdot cm^{-3})$	$(\mathbf{m} \cdot \mathbf{s}^{-1})$
	Ethanol + PPG	400	2-1	Propanol + PP	G400]	Ethanol + PPG4	400	2-H	Propanol + PPO	G400
0.0101	0.80010	T = 28	88.15 K	0 20025	1194.61	0.0101	0 78210	T = 31	8.15 K	0.77500	1080.08
0.0202	0.82267	1203.58	0.0101	0.81134	1194.54	0.0202	0.79688	1103.50	0.0101	0.78566	1090.57
0.0301	0.83465	1214.84 1225.54	0.0301	0.82471 0.83022	1204.43 1212.84	0.0301	$0.80896 \\ 0.82008$	1115.27 1126.60	0.0301	$0.79585 \\ 0.80465$	1100.81 1109.58
0.0500	0.85540	1235.28	0.0500	0.83887	1221.31	0.0500	0.82990	1136.43	0.0500	0.81335	1118.40
0.0600	0.86440 0.87312	1244.18 1253.25	0.0601 0.0702	$0.84688 \\ 0.85430$	1229.16 1236.68	0.0600 0.0705	0.83899	1145.92 1155.27	0.0601 0.0702	0.82140 0.82887	1126.44 1134.41
0.0905	0.88737	1268.18	0.1000	0.87340	1256.17	0.0905	0.86220	1170.52	0.1000	0.84821	1154.51
0.1497	0.91887	1301.79	0.1510	0.91806	1301.83	0.1497	0.89399	1204.63	0.2001	0.89320	1201.74
0.2005	$0.93701 \\ 0.95072$	1321.60 1336.87	$0.2500 \\ 0.3006$	0.93314 0.94561	$1317.71 \\ 1331.02$	0.2005	0.91257 0.92644	1224.36 1239.82	$0.2500 \\ 0.3006$	0.90849 0.92106	1217.70 1231.33
0.3000	0.96106	1347.92	0.3495	0.95551	1341.20	0.3000	0.93678	1250.57	0.3495	0.93107	1241.72
0.3309	0.98980	1369.57	0.4003	0.96416	1358.01	0.3309	0.94303	1272.26	0.4003	0.93979	1251.28
0.4991	0.98678 0.99113	1375.13	$0.4983 \\ 0.5492$	0.97729 0.98281	1364.34 1369.93	0.4991	0.96281	1277.47 1281 94	$0.4983 \\ 0.5492$	0.95313	1265.37 1270.89
0.6015	0.99462	1383.74	0.6008	0.98759	1375.17	0.6015	0.97068	1285.70	0.6008	0.96357	1276.29
0.6982	1.00008	1389.16	$0.6488 \\ 0.7008$	0.99157 0.99541	1379.58 1383.30	0.6982	0.97626 0.98085	1290.75 1295.14	$0.6488 \\ 0.7008$	0.96760 0.97153	1280.62 1284.39
0.8313	1.00580	1394.88	0.7991	1.00167	1389.90	0.8313	0.98209	1296.31	0.7991	0.97784	1291.17
0.8657	1.00772	1395.90	0.8274 0.8598	1.00320	1393.28	0.8657	0.98550	1297.05	0.8274 0.8598	0.97940	1292.00
0.9023	1.00825 1.00891	1397.10 1397.77	0.8930	1.00656 1.00761	1395.06 1395.95	0.9023	0.98457 0.98525	1298.29 1299.03	0.8930 0.9162	0.98284 0.98394	1296.10 1297.15
0.9458	1.00962	1398.25	0.9524	1.00923	1397.46	0.9458	0.98599	1299.27	0.9524	0.98556	1299.05
0.9831	1.010/1	1399.41	0.9805	1.01040	1398.89	0.9831	0.98707	1300.43	0.9805	0.98673	1299.97
0.0101	0.80058	1 - 29 1157.37	0.0101	0.79261	1149.88	0.0101	0.77422	1 - 52 1057.54	0.0101	0.76578	1044.69
0.0202	0.81419	1169.77	0.0199	0.80313	1160.19	0.0202	0.78798	1070.84	0.0199	0.77639	1055.10
0.0400	0.83725	1192.36	0.0399	0.81320	1178.63	0.0400	0.81125	1093.98	0.0399	0.79555	1074.56
0.0500	$0.84701 \\ 0.85603$	1201.94 1211.25	$0.0500 \\ 0.0601$	$0.83067 \\ 0.83868$	1187.20 1194.98	0.0500	0.82114 0.83024	1104.18 1113.49	$0.0500 \\ 0.0601$	0.80423 0.81235	1083.49 1091.97
0.0705	0.86479	1220.45	0.0702	0.84611	1202.97	0.0705	0.83909	1122.91	0.0702	0.81984	1099.89
0.0903	0.88512	1235.48	0.1510	0.89109	1222.51	0.0903	0.85966	1144.72	0.1510	0.86534	1120.20
0.1497	$0.91066 \\ 0.92915$	1268.99 1288.86	0.2001	$0.91006 \\ 0.92523$	1265.55 1284.18	0.1497	0.88554 0.90413	1172.59 1192.47	0.2001 0.2500	0.88451 0.89992	1168.31 1184.85
0.2506	0.94291	1304.36	0.3006	0.93770	1297.76	0.2506	0.91806	1207.88	0.3006	0.91253	1198.21
0.3000	0.95323 0.96188	1315.02 1324.64	0.3495 0.4003	0.94765 0.95630	1307.76	0.3000	0.92851 0.93736	1218.63 1228.54	0.3495 0.4003	0.92263 0.93139	1209.08 1218.60
0.4391	0.97321	1336.74	0.4515	0.96366	1324.57	0.4391	0.94880	1240.37	0.4515	0.93888	1226.61
0.5514	0.98331	1346.71	0.5492	0.97503	1336.44	0.5514	0.95896	1245.55	0.5492	0.95041	1238.91
0.6015	0.98682	1350.57 1355.68	$0.6008 \\ 0.6488$	0.97986 0.98384	1341.80 1346.22	0.6015	0.96248 0.96816	1253.83 1259.24	$0.6008 \\ 0.6488$	0.95533 0.95940	1244.04 1248.45
0.7996	0.99693	1360.31	0.7008	0.98774	1349.74	0.7996	0.97276	1263.29	0.7008	0.96338	1252.62
0.8637	0.99934	1362.42	0.7991	0.99407	1357.83	0.8637	0.97524	1265.59	0.8274	0.90970	1260.98
0.8856	1.00008 1.00060	1363.12 1363.33	$0.8598 \\ 0.8930$	0.99728 0.99894	$1359.59 \\ 1361.50$	0.8856	$0.97598 \\ 0.97655$	1266.20 1266.71	$0.8598 \\ 0.8930$	0.97307 0.97471	1262.93 1264.36
0.9230	1.00128	1364.18	0.9162	0.99999	1362.31	0.9230	0.97725	1267.40	0.9162	0.97588	1265.44
0.9458	1.00202	1365.55	0.9524 0.9805	1.00160	1364.21	0.9458	0.97800	1267.71 1269.00	0.9324 0.9805	0.97751	1267.20
		T = 30	08.15 K								
0.0101 0.0202	0.79196 0.80561	1123.88 1136.45	$0.0101 \\ 0.0199$	0.78402 0.79455	1115.08 1125.56						
0.0301	0.81765	1148.00	0.0301	0.80470	1135.60						
0.0400	0.82873	1169.01	0.0399	0.81348	1144.25 1152.92						
0.0600	0.84758	1178.50 1187.78	0.0601	0.83017	1160.73 1168 79						
0.0905	0.87070	1202.89	0.1000	0.85688	1188.57						
0.0998	0.8/6/6	1209.07 1236.77	0.1510 0.2001	0.88269 0.90170	1214.99						
0.2005	0.92091	1256.57	0.2500	0.91692	1250.85						
0.2300	0.94506	1271.95	0.3000	0.92930	1274.57						
0.3509	$0.95384 \\ 0.96509$	1292.17 1304.19	0.4003 0.4515	$0.94808 \\ 0.95548$	1284.13 1291.49						
0.4991	0.97095	1309.60	0.4983	0.96137	1298.08						
0.5514	0.97524	1314.09	0.5492	0.96690	1303.44						
0.6982	0.98435	1322.99 1327 42	$0.6488 \\ 0.7008$	0.97574 0 97965	1313.12 1316.80						
0.8313	0.99014	1328.54	0.7991	0.98593	1323.59						
0.8637	0.99135 0.99208	1329.25 1330.32	$0.8274 \\ 0.8598$	0.98753 0.98927	1324.89 1326.74						
0.9023	0.99260	1330.44	0.8930	0.99092	1328.67						
0.9250	0.99328	1331.45	0.9524	0.99360	1329.37						
			0.9805	0.99476	1332.18						

Table 3.	Dynamic	Viscosity	and Density	of Binary	Mixtures	Containing	Ethanol	+ PPG400	and 2	-Propanol	+ PPG40) at 1	Different
Tempera	tures												

<i>x</i> ₂	η (mPa•s)	$d (g \cdot cm^{-3})$	<i>x</i> ₂	η (mPa·s)	$d (g \cdot cm^{-3})$	<i>x</i> ₂	η (mPa•s)	$d (g \cdot cm^{-3})$	<i>x</i> ₂	η (mPa•s)	$d (g \cdot cm^{-3})$
Et	hanol + PPO	G400	2-P	ropanol + PI	PG400	Et	thanol + PPC	G400	2-P	ropanol + PF	PG400
		T = 29	98.15 K					T = 31	8.15 K		
$\begin{array}{c} 0.0059\\ 0.0125\\ 0.0199\\ 0.0278\\ 0.0370\\ 0.0470\\ 0.0576\\ 0.0705\\ 0.0885\\ 0.1035\\ 0.1248\\ 0.1483\\ 0.2010\\ 0.3003\\ 0.4037\\ 0.4826\\ 0.6051\\ 0.7063\\ 0.8070\\ 0.9083\\ \end{array}$	$\begin{array}{c} 1.187\\ 1.336\\ 1.444\\ 1.700\\ 1.942\\ 2.236\\ 2.468\\ 3.155\\ 3.568\\ 4.147\\ 4.939\\ 6.122\\ 9.173\\ 15.451\\ 22.820\\ 29.520\\ 39.413\\ 48.328\\ 55.757\\ 64.191 \end{array}$	T = 29 0.79461 0.80394 0.81379 0.82358 0.83400 0.84416 0.86475 0.87782 0.88730 0.89903 0.91002 0.92935 0.95334 0.96910 0.97756 0.98706 0.99278 0.99722 1.00083	 V8.15 K 0.0078 0.0163 0.0224 0.0361 0.0477 0.0604 0.075 0.0906 0.1046 0.1304 0.1550 0.2488 0.3005 0.3498 0.3096 0.4476 0.4994 0.5504 0.5504 0.6502 0.7004 	2.252 2.536 2.754 3.083 3.477 3.892 4.399 5.018 5.436 6.713 7.909 12.445 16.781 20.011 23.586 27.029 31.027 34.983 38.639 42.231 46.517	0.79006 0.79935 0.80565 0.81874 0.82874 0.83891 0.84951 0.85972 0.86799 0.88154 0.89282 0.92492 0.93767 0.94769 0.95619 0.96964 0.97513 0.97975 0.98397 0.98770	0.0059 0.0125 0.0199 0.0278 0.0370 0.0470 0.0576 0.0705 0.0885 0.1035 0.1248 0.1248 0.1483 0.2010 0.3003 0.4037 0.4826 0.6051 0.7063 0.8070 0.9083	$\begin{array}{c} 0.843\\ 0.922\\ 1.023\\ 1.143\\ 1.277\\ 1.480\\ 1.669\\ 1.761\\ 2.251\\ 2.481\\ 3.039\\ 3.489\\ 4.859\\ 7.485\\ 10.394\\ 12.758\\ 15.842\\ 18.541\\ 20.548\\ 22.962 \end{array}$	T = 31 0.77717 0.78656 0.79648 0.80633 0.81681 0.82704 0.83698 0.84776 0.86092 0.87047 0.88227 0.89332 0.91278 0.93696 0.95284 0.96136 0.97092 0.97666 0.98115 0.98479	8.15 K 0.0078 0.0163 0.0258 0.0361 0.0477 0.0604 0.075 0.0906 0.1046 0.1304 0.1550 0.3005 0.3498 0.3996 0.4476 0.4994 0.5504 0.5996 0.6502 0.7004 0.7492	$\begin{array}{c} 1.303\\ 1.468\\ 1.645\\ 1.784\\ 1.961\\ 2.221\\ 2.487\\ 2.796\\ 3.049\\ 3.605\\ 4.123\\ 7.628\\ 8.672\\ 10.245\\ 11.577\\ 13.497\\ 14.182\\ 15.100\\ 17.293\\ 17.200\\ 18.419\end{array}$	0.77253 0.78186 0.79158 0.80136 0.81140 0.82163 0.83229 0.84257 0.85089 0.86451 0.87585 0.92102 0.93111 0.93968 0.94674 0.95325 0.95880 0.96347 0.96347 0.96773 0.97150 0.97479
		T = 30	0.7492 0.7977 0.8466 0.9018 0.9491 08.15 K	50.723 54.740 58.666 62.363 66.945	$\begin{array}{c} 0.99097 \\ 0.99391 \\ 0.99660 \\ 0.99934 \\ 1.00146 \end{array}$			T = 32	0.7977 0.8466 0.9018 0.9491 28.15 K	19.367 20.747 22.098 22.724	0.97777 0.98049 0.98326 0.98542
0.0059 0.0125 0.0129 0.0278 0.0370 0.0576 0.0705 0.0885 0.1035 0.1248 0.1483 0.2010 0.3003 0.4037 0.4037 0.4826 0.6051 0.7063 0.8070 0.9083	$\begin{array}{c} 1.002\\ 1.11\\ 1.253\\ 1.397\\ 1.575\\ 1.799\\ 2.04\\ 2.352\\ 2.806\\ 3.198\\ 3.771\\ 4.568\\ 6.358\\ 10.165\\ 14.340\\ 18.215\\ 22.924\\ 27.825\\ 31.209\\ 35.063 \end{array}$	0.78596 0.79532 0.80521 0.81502 0.82548 0.83567 0.84558 0.85632 0.86943 0.87894 0.89071 0.90173 0.92112 0.94520 0.96099 0.96099 0.960948 0.97900 0.98473 0.98920 0.99283	0.00/8 0.0163 0.0224 0.0361 0.0477 0.0604 0.0750 0.0906 0.1046 0.1304 0.1304 0.1304 0.3095 0.3498 0.3996 0.4476 0.4994 0.5504 0.5996 0.6502 0.7004 0.7997 0.8466 0.9018 0.9491	$\begin{array}{c} 1.697\\ 1.886\\ 1.976\\ 2.322\\ 2.585\\ 2.895\\ 3.246\\ 3.648\\ 3.966\\ 4.784\\ 5.602\\ 10.660\\ 12.294\\ 14.301\\ 16.490\\ 18.335\\ 20.746\\ 22.568\\ 24.777\\ 26.564\\ 24.777\\ 26.564\\ 24.777\\ 26.564\\ 24.777\\ 26.564\\ 23.631\\ 34.635\\ 36.732\\ \end{array}$	0.78147 0.79077 0.79708 0.81019 0.82021 0.83040 0.84103 0.85127 0.85955 0.87312 0.88442 0.92943 0.93947 0.94799 0.95500 0.96148 0.96699 0.97164 0.97587 0.97963 0.98291 0.98587 0.98587 0.99133 0.99346	0.0059 0.0125 0.0125 0.0125 0.0278 0.0370 0.0576 0.0705 0.0885 0.1035 0.1248 0.1483 0.2010 0.3003 0.4037 0.4826 0.6051 0.7063 0.807 0.9083	0.704 0.799 0.866 0.971 1.083 1.226 1.627 1.627 1.887 2.049 2.524 2.917 3.800 6.034 7.862 9.493 11.301 12.535 13.780 15.407	0.76808 0.77764 0.78759 0.79745 0.80799 0.81827 0.82823 0.83903 0.85226 0.86188 0.87379 0.88488 0.90434 0.92866 0.94464 0.92866 0.94464 0.95317 0.96272 0.96852 0.97308 0.97677	0.0078 0.0163 0.0224 0.0361 0.0477 0.0604 0.0750 0.0906 0.1046 0.1304 0.1304 0.1304 0.3095 0.3095 0.3498 0.3996 0.4476 0.4476 0.4994 0.5504 0.5996 0.6502 0.7004 0.7997 0.8466 0.9018 0.9491	$\begin{array}{c} 1.043\\ 1.129\\ 1.247\\ 1.374\\ 1.515\\ 1.725\\ 1.887\\ 2.130\\ 2.364\\ 2.763\\ 3.134\\ 5.582\\ 6.409\\ 7.351\\ 8.137\\ 8.872\\ 9.885\\ 10.620\\ 11.525\\ 12.149\\ 13.008\\ 13.729\\ 14.445\\ 15.286\\ 16.037\\ \end{array}$	$\begin{array}{c} 0.76323\\ 0.77258\\ 0.77258\\ 0.77258\\ 0.77896\\ 0.79224\\ 0.80232\\ 0.81256\\ 0.82327\\ 0.8336\\ 0.84198\\ 0.85569\\ 0.86708\\ 0.91252\\ 0.92267\\ 0.93128\\ 0.92267\\ 0.93128\\ 0.92267\\ 0.93128\\ 0.92673\\ 0.95524\\ 0.95953\\ 0.95524\\ 0.95953\\ 0.96666\\ 0.96965\\ 0.97239\\ 0.97519\\ 0.97737\end{array}$

 x_2 , at T = (298.15 to 328.15) K are collected in Table 3. Plots of viscosity values versus polymer mole fraction are shown in Figure 3 for ethanol + PPG and 2-propanol + PPG systems. The results of $\Delta \ln \eta$ values calculated from eq 3 indicate that the deviation of logarithm of viscosity values is positive for the ethanol + PPG and 2-propanol + PPG systems over the entire composition range and over the four temperatures investigated.

Correlation. All the calculated values were correlated with the composition data by means of the Redlich–Kister polynomial, which for binary mixtures is

$$Q_{ij} = x_i x_j \sum_{k \ge 0} A_k (x_i - x_j)^k$$
(4)

where Q_{ij} is $V_{\rm m}^{\rm E}$, $\kappa^{\rm E}_{\rm s,m}$, or $\Delta \ln \eta$ and x_i is the mole fraction of component *i*. A_k is the polynomial coefficient, and *k* is the number of the polynomial coefficient. The adjustable parameters A_k determined by fitting the experimental values to eq 4 along with standard deviations of $V_{\rm m}^{\rm E}$, $\kappa^{\rm E}_{\rm s,m}$, and $\Delta \ln \eta$ are given in Tables

4 and 5 for the ethanol + PPG and 2-propanol + PPG systems, respectively. The full lines in Figures 1 to 3 correspond to the Redlich–Kister polynomials. On the basis of standard deviations reported in Tables 6 and 7, we concluded that the performance of the Redlich–Kister polynomial in the correlation of $V_{\rm m}^{\rm E}$, $\kappa_{\rm s,m}^{\rm E}$, and $\Delta \ln \eta$ values is good.

The $V_{\rm m}^{\rm E}$, $\kappa^{\rm E}_{\rm s,m}$, and dynamic viscosity, η , values of the studied systems were also correlated with the corresponding equation of the NRTL model. The NRTL equation for the excess molar volume and excess molar isentropic compression of solvent + polymer solutions has been taken from our previous work.⁶

In the correlation of the $V_{\rm m}^{\rm E}$ and $\kappa_{\rm s,m}^{\rm E}$ values of the investigated systems with the NRTL model,⁶ the smallest standard deviations were obtained using the value of 0.4 for the nonrandomness factor. To correlate $V_{\rm m}^{\rm E}$ and $\kappa_{\rm s,m}^{\rm E}$ data of a polymer solution with the NRTL model, its two parameters (τ_{12} and τ_{21}) are required which can be obtained from fitting of the vapor-liquid equilibrium, VLE, data to Chen's NRTL model¹⁰

Table 4. Parameters of the Redlich-Kister Polynomial, Equation 4, along with Standard Deviations, σ , of Binary Mixtures Containing Ethanol + PPG400 at Different Temperatures

<i>T</i> /K	A_0	A_1	A_2	A_3	A_4		σ
			V _n E	$m_{\rm m}^{\rm 2} ({\rm cm}^3 \cdot {\rm mol}^{-1})$			
						$\sigma(V_{\rm m}^{\rm E})$	$10^{3}\sigma(d)/(g \cdot cm^{-3})$
288.15	-3.349	1.757	-0.513	1.926	-2.116	0.01	0.06
298.15	-3.406	1.954	-0.947	1.759	-1.694	0.01	0.04
308.15	-3.519	2.091	-1.083	1.814	-1.717	0.01	0.05
318.15	-3.673	2.202	-0.926	1.896	-2.111	0.01	0.06
328.15	-3.787	2.432	-0.840	1.795	-2.591	0.01	0.06
			$\kappa^{\rm E}_{\rm s,m}/(6$	$cm^3 \cdot mol^{-1} \cdot kPa^{-1}$	1)		
						$10^7 \sigma(\kappa^{\rm E}_{\rm s.m})$	$\sigma(u)/(m \cdot s^{-1})$
288.15	-209.46	132.58	-81.58	166.81	-160.61	0.56	0.45
298.15	-239.74	151.61	-97.36	190.33	-183.77	0.66	0.47
308.15	-272.23	173.28	-114.50	224.63	-213.05	0.78	0.51
318.15	-307.77	198.58	-119.49	260.74	-264.10	0.94	0.55
328.15	-346.49	228.67	-128.50	308.88	-321.24	1.10	0.61
			Δ	$\ln \eta/(mPa \cdot s)$			
						$\sigma(\Delta \ln \eta)$	$\sigma(\eta)/(mPa \cdot s)$
298.15	4.982	-2.831	2.526	-2.006		0.02	0.31
308.15	4.576	-2.490	2.619	-2.742		0.02	0.26
318.15	4.389	-2.544	2.430	-2.306		0.02	0.15
328.15	4.305	-2.755	2.484	-2.366		0.02	0.16

Table 5. Parameters of the Redlich-Kister Polynomial, Equation 4, along with Standard Deviations, σ , of Binary Mixtures Containing 2-Propanol + PPG400 at Different Temperatures

T/K	A_0	A_1	A_2	A_3	A_4		σ
			$V_r^{\rm H}$	$m_{\rm m}^{\rm E}/({\rm cm}^3 \cdot {\rm mol}^{-1})$			
						$\sigma(V_{\rm m}^{\rm E})$	$10^{3}\sigma(d)/(g \cdot cm^{-3})$
288.15	-2.112	1.251	-0.223	0.649	-1.550	0.01	0.03
298.15	-2.163	1.252	-0.371	0.665	-1.508	0.01	0.03
308.15	-2.223	1.391	-0.482	0.643	-1.483	0.01	0.03
318.15	-2.320	1.437	-0.490	0.868	-1.577	0.01	0.03
328.15	-2.425	1.516	-0.690	1.154	-1.504	0.01	0.04
			$\kappa^{\rm E}_{\rm s,m}/($	$cm^3 \cdot mol^{-1} \cdot kPa^-$	1)		
						$10^7 \sigma(\kappa^{\rm E}_{\rm s.m})$	$\sigma(u)/(\mathbf{m} \cdot \mathbf{s}^{-1})$
288.15	-222.33	147.11	-93.21	161.89	-147.74	0.48	0.30
298.15	-255.79	168.73	-98.98	177.07	-192.58	0.54	0.32
308.15	-291.36	194.04	-114.23	202.66	-225.40	0.65	0.34
318.15	-333.15	223.10	-133.67	243.44	-260.77	0.72	0.35
328.15	-383.37	258.57	-162.90	304.36	-297.65	0.91	0.39
			Δ	$\ln \eta/(mPa \cdot s)$			
298.15 308.15	3.735 3.456	-2.005 -1.913	1.293 1.642	-0.794 -1.177		$ \begin{array}{c} \sigma(\Delta \ln \eta) \\ 0.02 \\ 0.01 \end{array} $	$\frac{\sigma(\eta)/(\text{mPa} \cdot \text{s})}{0.29}$ 0.17
318.15	3.446	-1.875	1.338	-1.993		0.02	0.28
328.15	3.284	-1.946	1.898	-1.221		0.01	0.09

Table 6. Parameters of the NRTL Model along with Standard Deviations, $\sigma(V_{\rm m}^{\rm E})$, for Ethanol + PPG400 and 2-Propanol + PPG400 Systems at Different Temperatures

Table 7.	Parameters of	the NRTL	Model along	with Standard
Deviation	is, $\sigma(\kappa^{\rm E}_{\rm s.m})$, for	Ethanol +	PPG400 and	2-Propanol +
PPG400 \$	Systems at Diff	erent Temp	peratures	

			$\sigma(V_{\rm m}^{\rm E})$	$10^3 \sigma(d)$
T/K	$10^4 \cdot \tau^{v}{}_{12}$	$10^4 \cdot \tau^{v}_{21}$	$(\text{cm}^3 \cdot \text{mol}^{-1})$	$(g \cdot cm^{-3})$
		Ethanol + PF	PG400	
288.15	-5.627	-0.174	0.02	0.11
298.15	-6.107	0.806	0.01	0.07
308.15	-6.623	1.530	0.01	0.06
318.15	-7.127	2.358	0.01	0.08
328.15	-2.846	-4.822	0.01	0.06
	1	2-Propanol + I	PPG400	
288.15	-5.347	2.017	0.01	0.06
298.15	-5.523	2.457	0.01	0.06
308.15	-6.275	2.769	0.01	0.05
318.15	-5.551	0.882	0.01	0.04
328.15	-9.253	8.603	0.01	0.06

for the systems studied. The values for τ_{12} and τ_{21} parameters at different temperatures have been taken from our previous work.¹¹

T/K	τ^{κ} 10	τ^{κ}	$(cm^3 \cdot mol^{-1} \cdot kPa^{-1})$	$(m \cdot s^{-1})$
	• 12	• 21	(••••••••••••••••••••••••••••••••••••••	(111 5)
		Ethanol	+ PPG400	
288.15	0.067	-0.048	0.73	0.44
298.15	0.079	-0.063	0.92	0.55
308.15	0.096	-0.081	1.03	0.57
318.15	0.113	-0.103	1.19	0.62
328.15	0.175	-0.134	0.79	0.34
		2-Propano	pl + PPG400	
288.15	0.106	-0.095	0.85	0.51
298.15	0.121	-0.115	1.22	0.65
308.15	0.177	-0.163	1.15	0.53
318.15	0.257	-0.214	0.91	0.36
328.15	0.224	-0.258	1.93	0.80

 $10^7 \sigma(\kappa^{\rm E}_{\rm s.m})$

 $\sigma(u)$

In the case of the NRTL equation, the required parameters $(\tau^{v}_{ij} \text{ and } \tau^{\kappa}_{ij})$ were obtained from fitting of V^{E}_{m} and $10^{7} \kappa^{\text{E}}_{\text{s,m}}$ data with the results collected in Tables 6 and 7, respectively.

Table 8. Parameters of the NRTL Model along with Standard Deviations, $\sigma(\eta)$, for Ethanol + PPG400 and 2-Propanol + PPG400 Binary Systems at Different Temperatures

		-	
T/K	$\tau^{\eta}{}_{12}$	$\tau^{\eta}{}_{21}$	$\sigma(\eta)/(mPa.s)$
	Ethanol	+ PPG400	
298.15	-1.970	0.396	0.20
308.15	-2.267	1.635	0.15
318.15	-1.599	0.598	0.07
328.15	-0.989	0.192	0.11
	2-Propan	ol + PPG400	
298.15	-1.686	0.538	0.25
308.15	-1.967	1.579	0.13
318.15	-1.700	1.402	0.41
328.15	-1.492	1.254	0.10

The dynamic viscosity data have been correlated with the segment-based Eyring–NRTL viscosity model, proposed recently by Novak et al.¹² In the correlation of the dynamic viscosity of the investigated systems with the Eyring–NRTL model,¹² the smallest standard deviations were obtained using the value of 0.25 for the nonrandomness factor. The two parameters of the segment-based Eyring–NRTL viscosity model, τ^{η}_{12} and τ^{η}_{21} , were obtained by using the dynamic viscosity data from Table 3, and these parameters are collected in Table 8 for the ethanol + PPG and 2-propanol + PPG systems.

To see the performances of the Redlich–Kister and NRTL models, comparison between the experimental and calculated $V_{\rm m}^{\rm E}$, $\kappa_{\rm s,m}^{\rm E}$, and η values is shown, respectively, in Figures 1 to 3. As can be seen from these figures and standard deviations reported in Tables 4 to 8, the performance of the NRTL model with only two parameters in the correlation of $V_{\rm m}^{\rm E}$ or $\kappa_{\rm s,m}^{\rm E}$ values is similar to that of the Redlich–Kister equation with five adjustable parameters. The quality of fitting of η values with the NRTL model with only two parameters is better than the Redlich–Kister polynomial with four adjustable parameters.

Conclusion

Experimental density, speed of sound, and dynamic viscosity data were obtained for ethanol + PPG and 2-propanol + PPG systems over the entire range of compositions at different temperatures. The excess molar volume and excess molar isentropic compression values, calculated from these experimental data, are negative, whereas deviations of logarithm of viscosity values are positive. The Redlich–Kister polynomial and NRTL model were applied successfully for the correlation of V_m^E , $\kappa_{s,m}^E$, and $\Delta \ln \eta$ values. The quality of fitting of excess volume or excess molar isentropic compression values for the studied systems with the NRTL model with only two parameters is similar to that of the Redlich–Kister polynomial with five parameters. In the case of correlation of viscosity values, it was found that the performance of the NRTL model is better than the Redlich–Kister polynomial.

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